NOTIZEN

Tracer Impurity Diffusion in Liquid Metals: K in Na and Na in K

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The diffusivities of ^{42}K in Na and of ^{24}Na in K have been measured between 100 ° and 285 °C, utilizing an „infinite capillary" technique. The results are adequately described by the Arrhenius relations (in cm²/s) $D_{\text{K in Na}} = 0.46 \cdot 10^{-3} \exp(-1.82/RT)$ and $D_{\text{Na in K}} = 0.93 \cdot 10^{-3} \exp(-2.11/RT)$. The differences ΔQ in effective activation energies between impurity diffusion and self-diffusion are about −0.4 kcal/mole for Na and +0.1 kcal/mole for K. This can be satisfactorily explained by electrostatic screening arguments. The impurity diffuses slower than the host atoms in Na, faster in K.

The self-diffusion behaviour of the liquid alkali metals has been charted by Larsson et. al.[1] and given a model interpretation by Lodding [2]. The model is based on the postulate of characteristic frequencies and energies of vibration, assuming also that all non-vibration energy is diffusive. While a liquid counterpart of the Debye frequency can be readily formulated for the solvent, the local oscillation and displacement frequencies of the impurity-solvent complex are less easy to estimate, being dependent not only on the solute mass but also on the size and effective excess charge. In the solid state, diffusion theories have become established for homovalent [3] as well as heterovalent [4] impurities in metals. The theory is successful for systems where vacancy diffusion dominates. The liquid can be considered to contain excess free volume [5, 6, 7], possibly a large concentration of "smeared-out" vacancies. It is of interest to see to what extent the solid-state arguments regarding ΔQ (i. e. $Q_i - Q_0$, the difference in activation energy between impurity and solvent diffusion) can be applied to liquids.

Rather few data have hitherto been obtained on impurity diffusion in liquid metals. Heterovalent impurities in Ag have been studied by Leak and Swalin[8], Au in Ag by Gupta [9] and In in Ga by Eriksson [10] & al. The choice of system in the present investigation is motivated by the availability of accurate self-diffusion data in Na and K[1], by the technical interest in liquid NaK, and by abundant theoretical work on various properties of liquid alkalis.

The capillary method used in this investigation has been developed for liquid Ga [11, 12, 10] and subsequently tested on In [13]. For Ga the method was "non-destructive", i. e. the activity could be continuously scanned by means of a collimator in front of the crystal. In the present case it was impossible to obtain sufficient radioactive intensity to allow the use of a collimator. Instead the capillaries were sectioned after anneal, prior to counting. This alternative had also been tried for Ga self-diffusion and found to alter the reproducibility of the results from some 2 % to 5 % in D.

The K metal was 98 %, the Na metal 99.9 % pure and further cleaned from oxide by pressing the melt through a sinter mesh before collection in a long glass "finger". For each run a 1 cm long piece was cut off. The metal surface in the open end of the finger was between runs protected from excessive oxidation by immersion in a volatile oil containing a few grains of water absorbant. The freshly cut section was quickly introduced into the wide part of the cell above the valve (Fig. 2).

The ^{24}Na and ^{42}K tracers were obtained by irradiation, in the Studsvik R2 reactor, of especially pure matrix metal steeped in 2 cm long, 0.6 mm o. d. quartz capillaries.

After evacuating the cell to 10^{-4} torr the tracer was introduced into the cell through its side arm by cutting off a piece of the 0.6 mm quartz capillary inside the apparatus shown in Fig. 1. The cut-off capillary fragment with active metal was allowed to fall under vacuum into the capillary of the cell, arriving at its closed end. The inactive matrix metal was let in through the vacuum lock, melted and permitted to run down to the mouth of the capillary, the oxide crust remaining in the finger section. The shiny metal was then pushed into the capillary by replacing vacuum with atmospheric pressure of SR quality argon.

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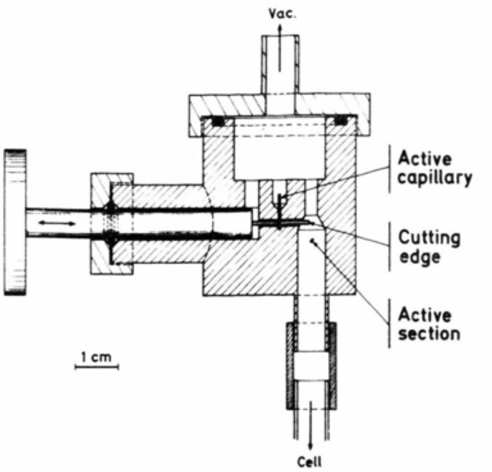

Fig. 1. Apparatus for cutting the quartz capillary with activated metal.

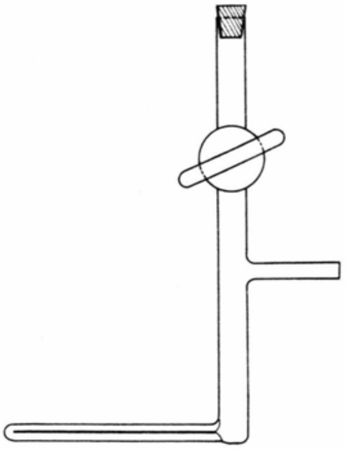

Fig. 2. Pyrex glass cell

The anneal then proceeded analogously to Ref. [12]. After cooling, the capillary with solidified metal was cut into about 5 mm long sections and the activity of each was determined by means of a single channel analyzer with a well-type NaJ crystal. The diffusion profile corresponded to the solid-state thin film geometry [12]. A correction, of the order of 2 to 20 % in D, was made for the contraction of the column in melting and in solidification [1].

In Fig. 3 the results are shown graphically on a linear scale. The results may be equally well represented by a Arrhenius type expression, $D = D_0 \exp(-Q/RT)$. The parameters, as obtained by least squares analysis of the experimental data in Fig. 3, are listed in Table 1, where they are compared with those of self-diffusion of the solvents. The solute-solvent difference in "activation energy", ΔQ, is seen to be (–0.40 ± 0.20) for diffusion in the Na matrix, and (+0.09 ± 0.23) in K. Further, it is readily seen from Fig. 3 that in spite of the lower "activation energy" K in Na diffuses slower than Na in Na, and despite the positive ΔQ in K the Na impurity diffuses faster than the K host.

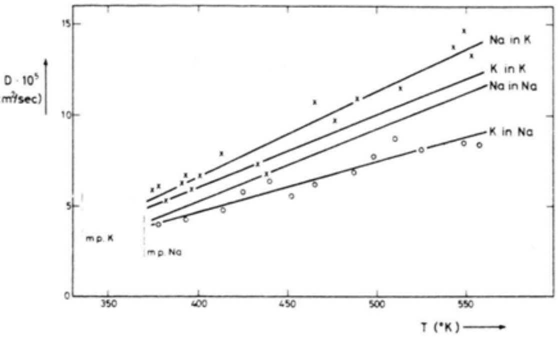

Fig. 3. Plot of diffusion coefficients in liquid Na and K versus absolute temperature. The straight lines for Na in Na and K in K are taken from [1].

The behaviour of K in Na is quite analogous to that of In in Ga [10]. As in Ref. [10] it seems reasonable to assume that the negative ΔQ is due to the greater ability of the relatively electropositive solute to attract voids, while the smaller D values follow from the relatively great impurity mass. By the same argument the "opposite" results for Na in K are intuitively understandable. In the study of Au in Ag [9] the heavy and relatively electronegative impurity exhibited the faster diffusion as well as the greater "activation energy", but the former effect was uncertain within the accuracy margins.

LECLAIRE's homovalent impurity theory gives a quantitative prediction of the solute-solvent difference E in vacancy formation energy next to the diffusing atom. The complete ΔQ term also contains migration energy and correlation terms, but by most models of liquid diffusion [6, 7, 2] these ought to be small. The remaining term, ΔE, is via a constant related to an effective valence difference ΔZ, which can be calculated from known solute-solvent differences in Fermi-, sublimation- and ionization energies. When the Thomas Fermi interatomic potential model is applied to the alkali metals, one predicts $\Delta E = -0.40$ for K in Na, and +0.29 for Na in K. The first value agrees strikingly with our experimental result, the second one is within the margins of error. Similar agreement with the solid-state theoretical ΔE has been found in other studies [8–10] of impurity diffusion in liquid metals. It then appears that although the diffusion-furthering voids may assume a wide range of sizes and shapes in the liquid, the electrostatic screening arguments proposed for solid-state vacancies [14, 3] can still be applied.

A recent model, devised specifically for liquid diffusion [2], predicts a linear temperature dependence, according to $D = A\,(T-B)$, where A entails the mass, and B is related to the heat and temperature of melting.

The model has been extended to impurity diffusion [2a]. In view of a discussion to follow in [2a] the experimental values of A and B are listed in Table 1.

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Table 1. Arrhenius and linear parameters for diffusion in liquid Na and K.

System	$D_0 \cdot 10^3$(cm²/s)	Q (kcal/mole)	$A \cdot 10^7$cm² s⁻¹grad⁻¹	B(°K)
K in Na	0.46±0.12	1.82±0.12	2.72±0.28	225±20
Na in Na	0.86±0.09	2.22±0.08	3.90±0.13	263± 9
Na in K	0.93±0.19	2.11±0.16	4.75±0.30	261±15
K in K	0.76±0.06	2.02±0.07	3.89±0.11	244± 9

The ratio of the nuclear g_I-factors of ^{95}Mo and ^{97}Mo

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With a multi-nuclei Fourier transform NMR spectrometer the ratio of the Larmorfrequencies of ^{95}Mo and ^{97}Mo in a solution of K_2MoO_4 in H_2O has been measured with high accuracy. Using hyperfine interaction constants from literature, we have calculated the hyperfine structure anomaly $^{95}\Delta^{97} = -0.0102(14)$% of molybdenum in the atomic ground state $4d^55s\ ^7S_3$.

Introduction

For many isotopic pairs values of the hyperfine structure anomaly (HFSA) have been quoted [1]. For the two stable odd isotopes of molybdenum ^{95}Mo and ^{97}Mo recently Pendlebury and Ring [2] have measured the magnetic hyperfine interaction constants in the $4d^55s\ ^7S_3$ atomic gound state: $A(^{95}\text{Mo}) = -208.5790$ (20) MHz, $A(^{97}\text{Mo}) = -212.9781(20)$ MHz. Together with the ratio of the g_I-factors of Proctor and Yu [3], which has an accuracy of only $1 \cdot 10^{-4}$, Pendlebury and Ring [2] gave a value of the HFSA in the atomic ground state: $^{95}\Delta^{97} = -0.01(1)$ %. The error results from the NMR measurement of Proctor and Yu [3]. If one therefore knows the ratio of the g_I-factors, which is equal to the ratio of the Larmor-frequencies, with an accuracy of at least $1 \cdot 10^{-5}$, one can get a more meaningful value of the HFSA of the molybdenum isotopes ^{95}Mo and ^{97}Mo. A nonvanishing value of the HFSA can give information about both the electronic configuration and some nuclear properties.

The Hyperfine structure anomaly

The HFSA of two isotopes 1 and 2 is defined by

$$^1\Delta^2 = (A_1/A_2) \cdot (g_{I_2}/g_{I_1}) - 1 . \qquad (1)$$

A_1, A_2 are the experimental magnetic hyperfine interaction constants of the atomic state in question; g_{I_1}, g_{I_2} are the nuclear g-factors. The value of Δ is usually given in %.

The magnetic hyperfine interaction constant, can be written as:

$$A = A_{\text{point}}\,(1 - \delta)\,(1 - \varepsilon) , \qquad (2)$$

where A_{point} is the hyperfine interaction constant, that one would get, if the observed nucleus were a point nucleus, δ is a correction considering the distribution of the electric charge over the volume of the nucleus [4, 5, 6] and ε is a correction considering the distribution of the magnetization [7–10]. δ and ε take values of a few percents for $s_{1/2}$ and $p_{1/2}$ electrons; in other electronic states, if relativistic effects and effects of configuration mixing can be neglected, one finds: $\delta = \varepsilon = 0$. Taking into account the definition of A_{point} one gets the following equation for the HFSA

$$^1\Delta^2 = \frac{(1 - \delta_1)\,(1 - \varepsilon_1)}{(1 - \delta_2)\,(1 - \varepsilon_2)} - 1 , \qquad (3)$$

if reduced mass effects can be neglected. This is the case for the two molybdenum isotopes. ε_1, ε_2, δ_1, δ_2 are the corrections for the respective isotope 1 or 2.

Therefore Eqn. (1) can be written in a fairly good approximation as:

$$^1\Delta^2 \approx (\delta_2 - \delta_1) + (\varepsilon_2 - \varepsilon_1) = \Delta_\delta + \Delta_\varepsilon . \qquad (4)$$

Eqn. (4) shows the physical meaning of the HFSA.

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Measurement of the ratio of the Larmor frequencies

The NMR signals of the molybdenum isotopes have been detected in a field of 1.807 tesla by a Bruker B-KR 322s pulse spectrometer. The signals were enhanced by a Hewlett-Packard signal analyzer 5480 A and the Fourier transformation was computed on the CDC 3300 of the Zentrum für Datenverarbeitung der Universität Tübingen. The magnetic field was held constant with the aid of a ^{7}Li NMR probe [11].

^{97}Mo has relatively short relaxation times [12]. The Fourier transformation of the free induction decay yields the Larmorfrequency. The linewidth of the NMR signal of ^{97}Mo of 100 Hz is partly due to the inhomogeneity of the magnetic field and partly due to relaxation processes.

Though both isotopes have nuclear spin $I = 5/2$, ^{95}Mo has long relaxation times [12]. Therefore a special technique, the so-called Quadriga Fourier transform Spectroscopy of SCHWENK [13] was used for recording the NMR signal of ^{95}Mo. The linewitdth of 60 Hz of this signal is due to the used technique.

The Larmor frequencies of ^{95}Mo (about 5.014 MHz) and of ^{97}Mo (about 5.119 MHz) were measured alternately in the same probe and sample (10 mm tube diameter) only by varying the excitation frequency, at a temperature of (301 ± 3) K. The sample was a 3 molal solution of K_2MoO_4 in H_2O. For the NMR signal of both molybdenum isotopes a signal to noise ratio of 50 was achieved, within summation times of about 6 minutes.

We have measured 67 ratios of the Larmor-frequencies of ^{95}Mo and ^{97}Mo at four different days. The result is:

$$\nu(^{95}\mathrm{Mo}) \,/\, \nu(^{97}\mathrm{Mo}) = 0.979\,445\ (1)$$

All the measured ratios lie within the given limits of error.

PROCTOR and YU [3] gave the following value of that ratio:

$$\nu(^{95}\mathrm{Mo}) \,/\, \nu(^{97}\mathrm{Mo}) = 0.9794(1)$$

These values are in agreement within their limits of error.

The HFSA of ^{95}Mo and ^{97}Mo

Using the A-factors of PENDLEBURY and RING [2] of the atomic ground state 4d^{5}5s $^7S_3$ and our ratio of the Larmor frequencies of ^{95}Mo and ^{97}Mo we get for the HFSA:

$$^{95}\Delta^{97}\ (4d^5 5s\ ^7S_3) = -0.0102(14)\%.$$

The HFSA is relatively large because of the dominant contribution of the unpaired s-electron to the A-factor. The error results from the measurement of PENDLEBURY and RING [2]. ROSENTHAL and BREIT [4] and CRAWFORD and SCHAWLOW [5] have given a formula for δ based on the assumption, that the nuclear radius varies proportional to (number of nucleons) $^{1/3}$ and that the charge distribution is constant over the nuclear volume. From this formula one gets for a $s_{1/2}$ electron in the case of molybdenum:

$$\Delta_\delta = 0.016\%.$$

ROSENBERG and STROKE [6] have used a more realistic model of the distribution of the electric charge. They get for a $s_{1/2}$ electron in the case of molybdenum:

$$\Delta_\delta = 0.007\%.$$

If one assumes, that the HFSA of molybdenum is wholly due to the 5s electron, one can calculate from Eqn. (4) the contribution to the HFSA, which is due to the distribution of the magnetization over the volume of the nuclei. We get:

$$\Delta_\varepsilon = -0.017\%.$$

One can see, that we get a relatively large contribution to the HFSA, though the magnetic moments of both isotopes are only 2 % different from each other.

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